Model System Diagnostics for High-Energy Cathode Development

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2019 DOE VTO Annual Merit Review
June 13, 2019

Project ID: bat225

Overview

Timeline

- Start date: October 2016
- End date: September 2019
- Percent complete: 90%

Barriers Addressed

- Energy density
- Cycle life
- Safety

Budget

- Total project funding
  - FY2018 $500K
  - FY2019 $500K

Partners

- Interactions/collaborations: LBNL, UCB, ANL, Cambridge, ORNL, PNNL, NCEM, ALS, SSRL
- Project lead: Vincent Battaglia

Relevance/Objectives

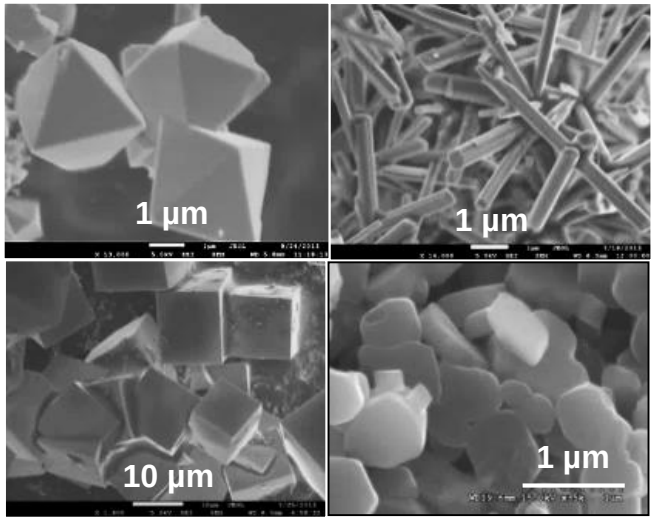
- Obtain fundamental understanding on performance-limiting properties, phase transition mechanisms, kinetic barriers, and instabilities in high-energy cathode materials
- Develop strategies to improve solid-state charge transport and optimize charge transfer at electrode-electrolyte interface
- Discover and develop next-generation electrode materials based on rational design as opposed to the conventional empirical approaches

Milestones

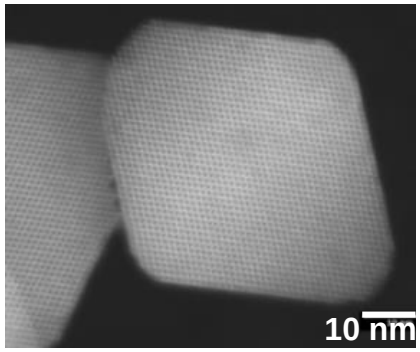
Date	Milestones	Status
December 2018	Understand the interplay between cationic and anionic redox processes in model transition-metal (TM) oxides.	Completed
March 2019	Characterize interfacial processes and surface changes on anion-active model oxides.	Completed
June 2019	Evaluate the effect of particle size/morphology on oxygen redox chemistry and kinetics.	On schedule
September 2019	Develop design strategies to improve performance of anion-active oxide cathodes.	On schedule

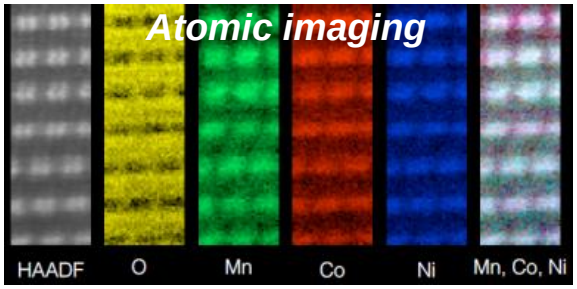
Approach/Strategy

High-quality model samples with well-controlled physical properties

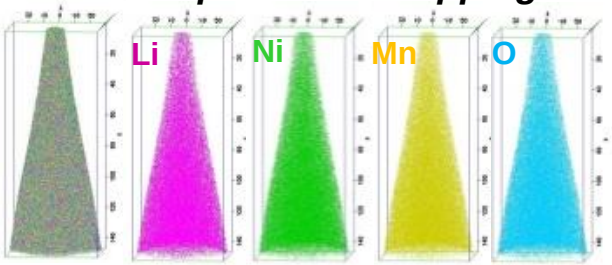


Fundamental understanding of solid-state chemistry, kinetic barriers and instabilities during battery operation





3D compositional mapping



Model-system construction

Advanced diagnostics

Rational design, synthesis and testing of materials

Fundamental knowledge

Technical Accomplishments: Overview

I. Fundamental understanding of anionic redox in Li-rich TM (LRTM) oxides and its impact on cathode performance

a) Collective redox activities of TM cations and oxygen anions responsible for high capacity in LRTM oxide cathodes

b) O redox increases capacity but reduces cycling stability and rate capability

II. What influences stability of LRTM oxide cathodes with O redox?

a) Bulk strategies to increase stability of O redox

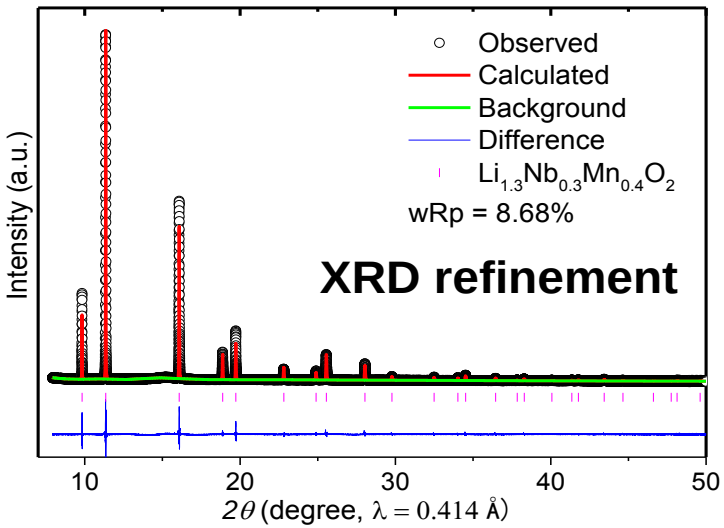
- Effect of redox-inactive TM
- Effect of anion substitution

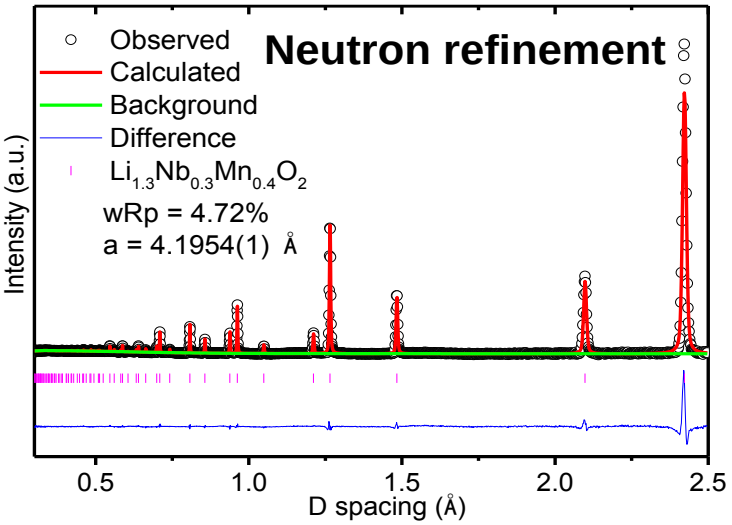
b) Surface engineering approaches to stabilize anion-active LRTM oxides

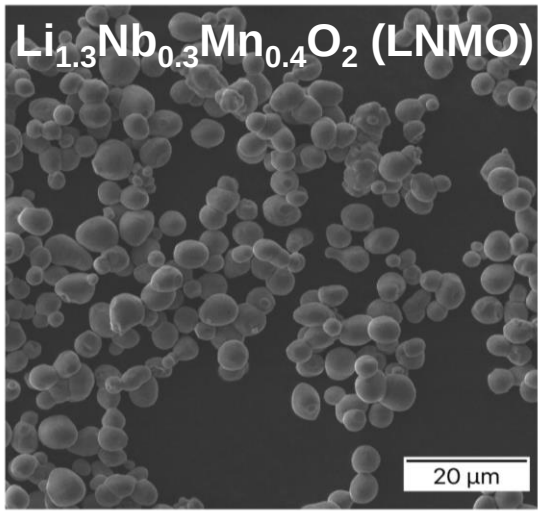
- Synthesis of LRTM oxides stabilized by surface segregated TM
- Post-synthesis surface coating

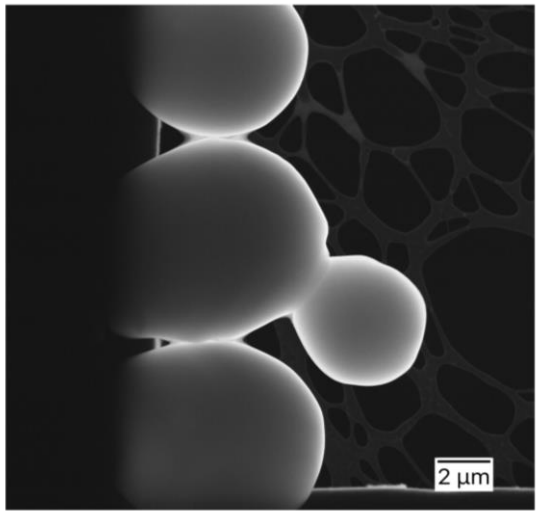
This presentation only focuses on I) and II a)

LRTM oxide single crystals synthesized





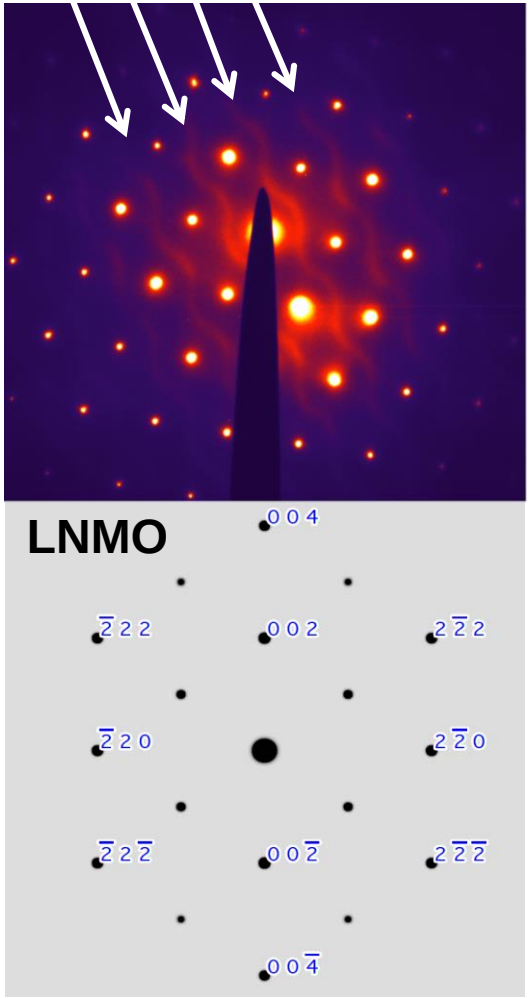




- Phase-pure crystal samples of $Li_{1+x}(M'Mn)_{1-x}O_2$ ($0.2 \le x \le 0.4$, M' = Nb, Ta, Ti, W, Zr, or combinations of) rock-salts synthesized by using a molten-salt method.

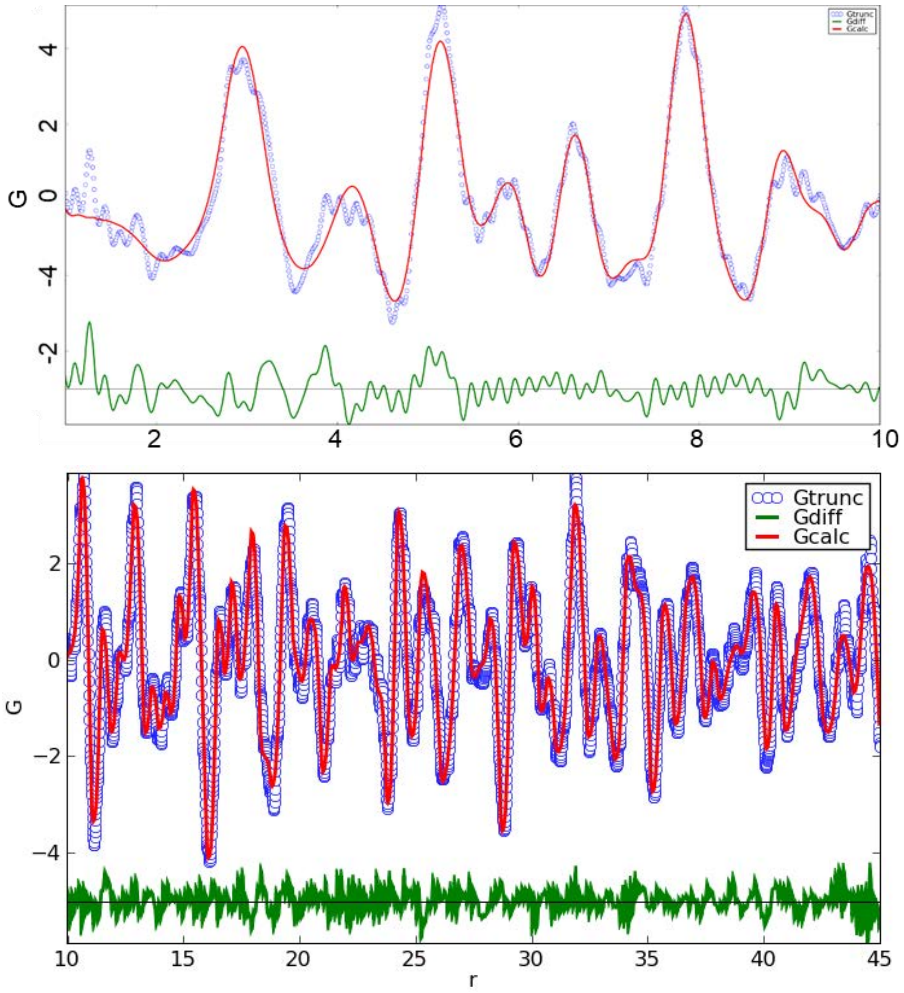
Local short-range ordering observed in Cation-disordered rock-salt structure

Evidence for local short-range ordering at particle-level (TEM/EDX, NCEM)



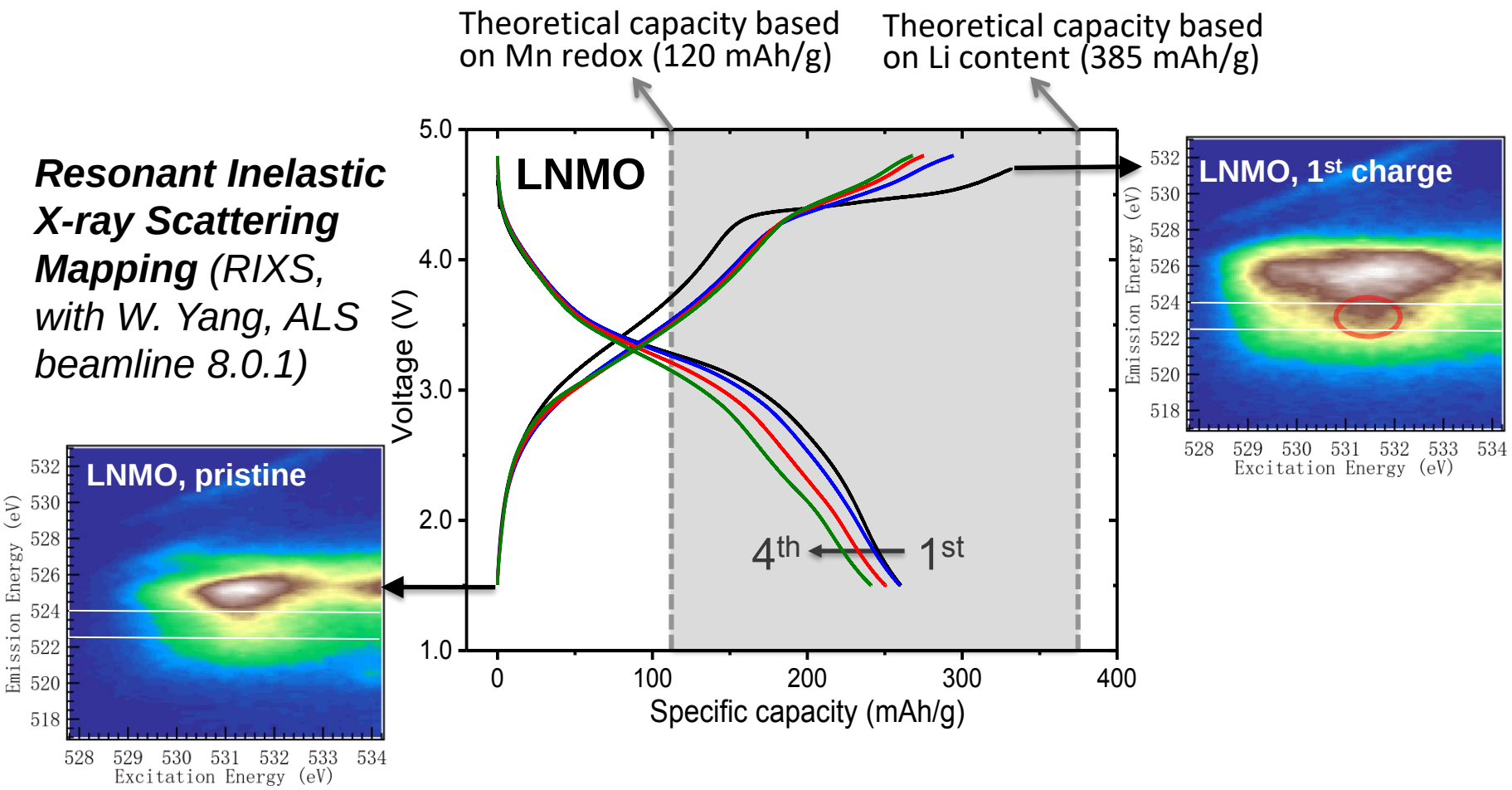
Neutron PDF analysis
(NOMAD at SNS/ORNL)

G. Chen et. al, *Chem* **4** (9), 2108 (2018)



Combined TM and O redox leads to high capacity

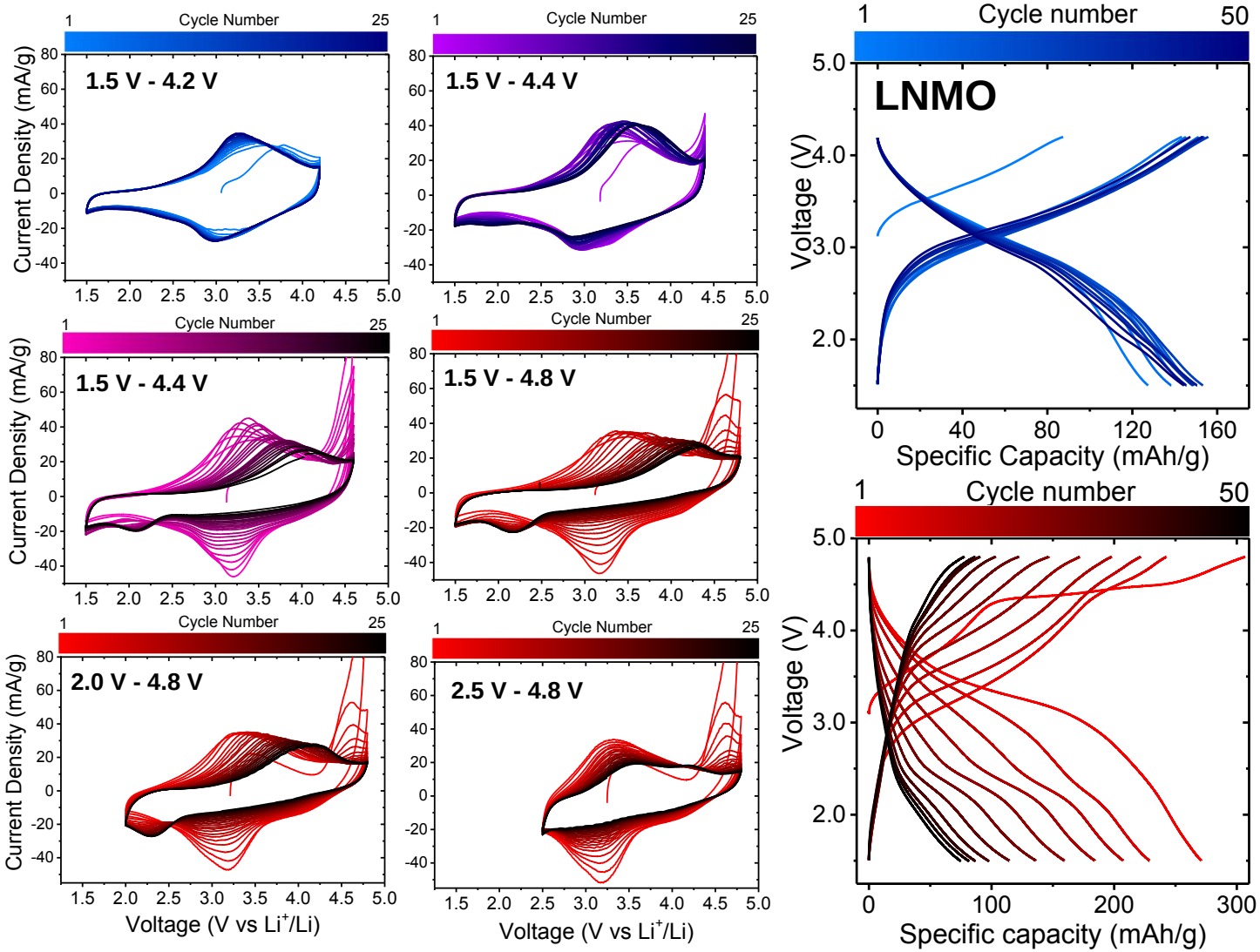
Resonant Inelastic X-ray Scattering Mapping *(RIXS, with W. Yang, ALS beamline 8.0.1)*



- Mn redox contributes 120 mAh/g with 0.4 Li^+ extraction at lower voltages.
- O redox contributes 140 mAh/g at higher voltages.

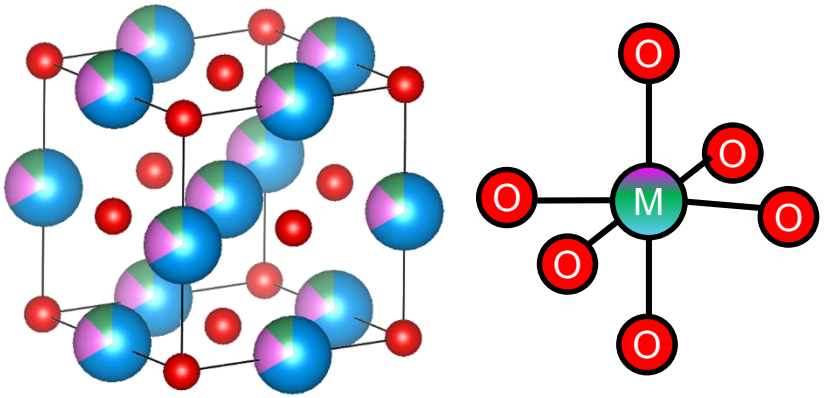
G. Chen et. al, *Chemistry of Materials* **30**, 1655 (2018)

Cycling stability correlated to extent of O redox



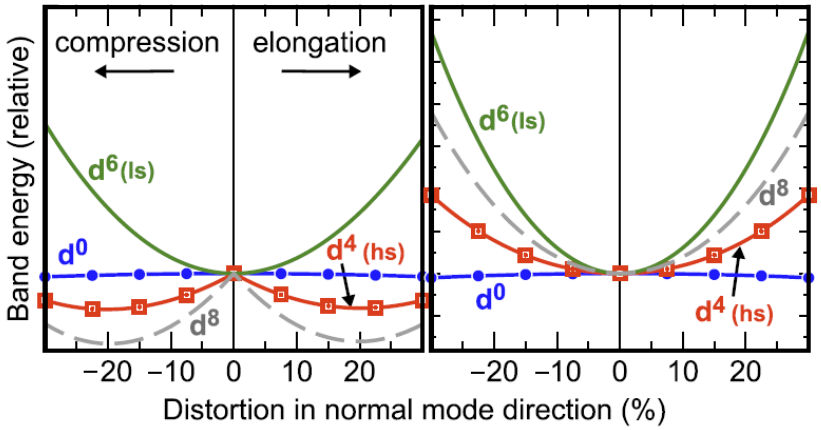
- Cycling capacity increases while stability (capacity and average discharge voltage) decreases with increasing involvement of O redox at high voltages.

Influence of redox-inactive TM

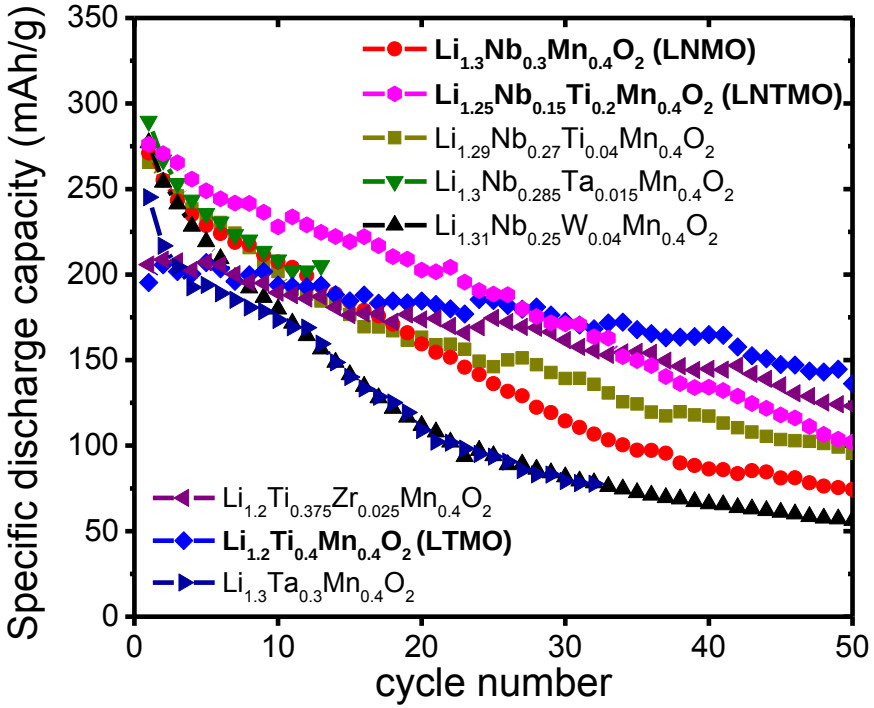


M = Li and TM (redox active and inactive)

$Li_{1+x}(M'Mn)_{1-x}O_2$ (redox-inactive M' = Nb, Ta, Ti, W, Zr, or combinations of, $0.2 \le x \le 0.4$)



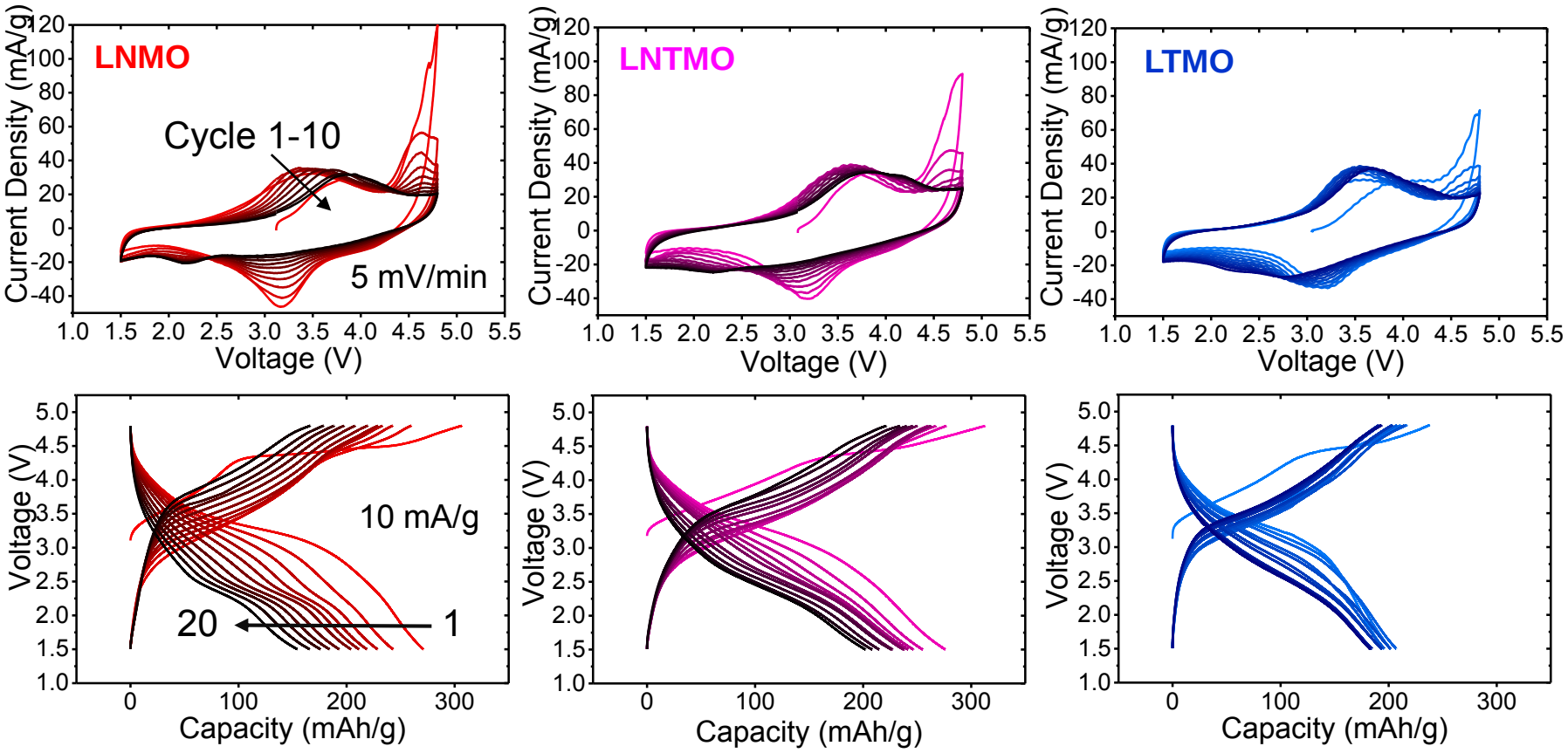
A. Urban et. al, Phys. Rev. Lett. 119, 176402 (2017)



- Redox-inactive TMs are d^0 TMs (Ti^{4+}, Mo^{6+}, V^{5+}, Nb^{5+}, Zr^{4+} etc.) essential in formation of disordered rock-salt crystal structure.

- Redox-inactive TMs also have a critical role in electrochemical performance of LRTM oxides.

Redox-inactive TM influences cycling stability

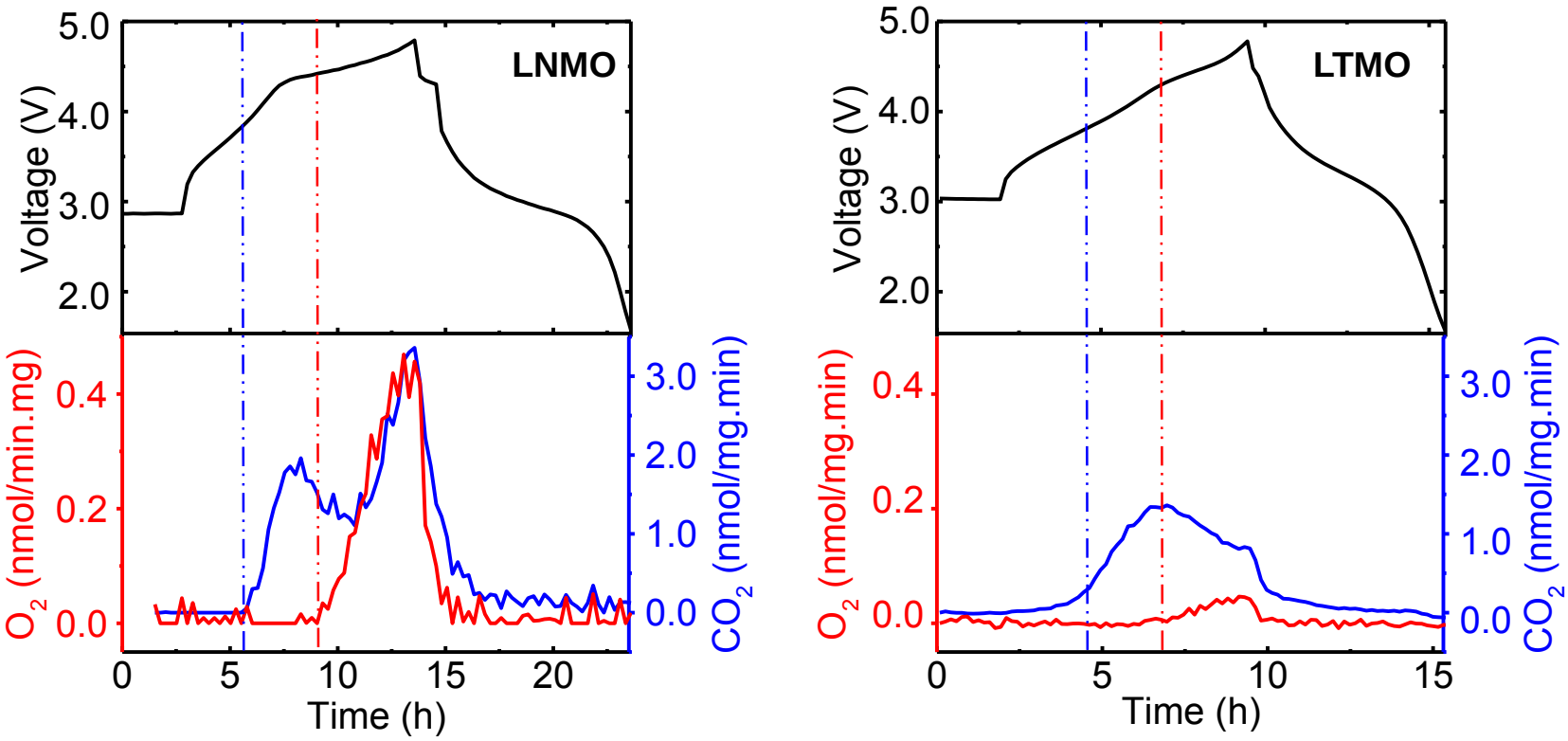


- Samples with the same redox-active Mn content but varying redox-inactive TMs were selected for further evaluation: $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ (LNMO), $Li_{1.25}Nb_{0.15}Ti_{0.2}Mn_{0.4}O_2$ (LNTMO) and $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$ (LTMO).
- Redox-inactive Ti provides stabilizing effect in electrochemical performance of oxide cathodes.

Redox-inactive TM influences O loss

Operando Differential Electrochemical Mass Spectroscopy

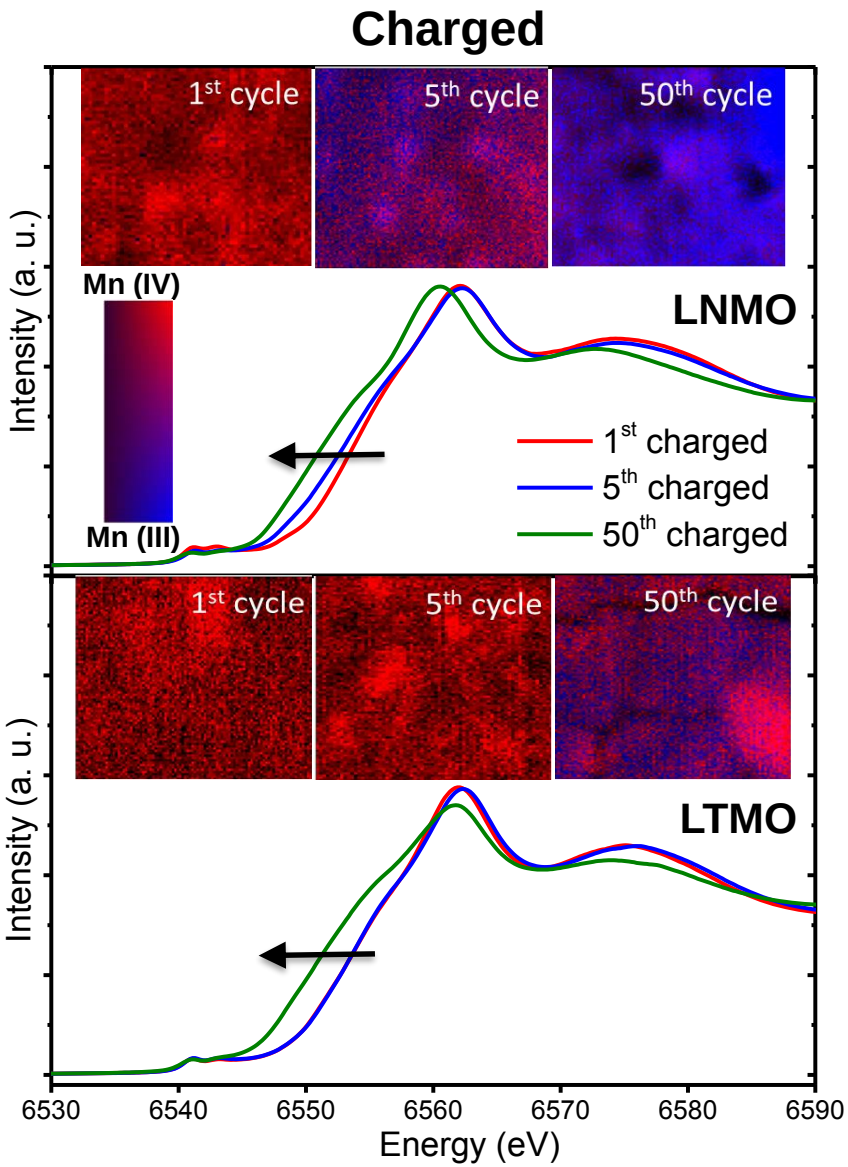
(DEMS, with B. McCloskey, UC Berkeley)

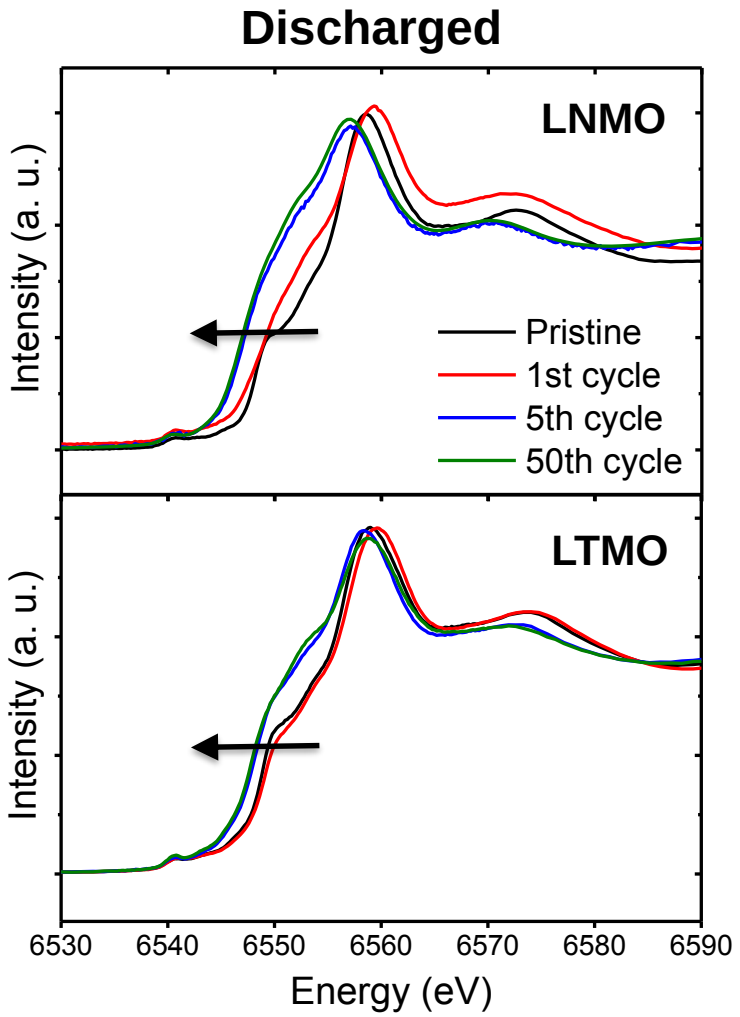


- Oxygen gas release detected upon first charge to ~ 4.3 V.
- Oxygen loss in LTMO is ~ 10x less compared to that in LNMO.

Redox-inactive TM influences chemical stability

Mn K-edge hard XAS spectra/mapping *(SSRL beamline 2-2)*





- Cycling-induced bulk Mn reduction less severe in LTMO.

Responses to Previous Year Reviewers' Comments

No reviewer comments received from 2018 DOE Merit Review

Collaborations

- Prof. Gerd Ceder and Kristin Persson (UC Berkeley) – modeling
- Drs. Marca Doeff (LBNL), Dennis Nordlund and Yijin Liu (SSRL), and APS – synchrotron *in situ* and *ex situ* XRD, XAS and FF-TXM-XANES studies
- Dr. Wanli Yang (ALS) – synchrotron XAS and RIXS studies
- Prof Bryan McCloskey (UC Berkeley) – DEMS
- Drs. Jagjit Nanda, Ashfia Huq (ORNL) and Jack Chen (Chinese Academy of Sciences, CAS and ANSTO) – neutron diffraction and PDF studies
- Dr. Chongmin Wang (PNNL) – STEM/EELS

ALS ADVANCED LIGHT SOURCE

SSRL

Berkeley UNIVERSITY OF CALIFORNIA

Pacific Northwest NATIONAL LABORATORY

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Advanced Photon Source ARGONNE NATIONAL LABORATORY

OAK RIDGE NATIONAL LABORATORY MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

CHINESE ACADEMY OF SCIENCES

Australian Government ANSTO

Remaining Challenges and Barriers

- Comprehensive understanding on the selection rules of redox-active and redox-inactive TMs in LRTM oxides necessary in order to optimize composition for cathode performance and stability.
- Surface chemistry of LRTM oxides – rock-salt nature of the samples makes it difficult to effectively monitor the formation of surface layer due to O loss and TM migration as well as its evolution with cycling.
- Further fundamental understanding of performance limiting mechanisms/processes in newer LRTM oxide cathodes needed in order to evaluate how O redox can be utilized to develop commercially viable high-energy cathodes

Proposed Future Work

- Obtain further understanding on the interplay between cation and anion redox processes in LRTM oxides and how redox-inactive TM modulate O redox and overall stability.
- Explore techniques to investigate surface chemistry of LRTM oxides, particularly the formation of surface layer due to O loss and TM migration, how the layer thickness evolves with cycling and what impact it has on cathode performance.
- Develop strategies to design and protect LRTM oxide surface against side reactions (particularly oxygen loss), chemical and structural instabilities.
- Obtain comprehensive understanding on performance limiting mechanisms/processes in LRTM oxide cathodes and develop mitigating approaches to address the identified issues.
- Provide material design insights on how to balance capacity and stability of LRTM oxide cathodes.

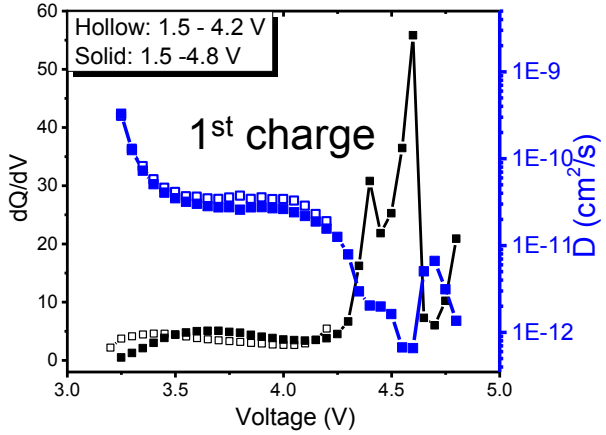
"Any proposed future work is subject to changes based on funding levels."

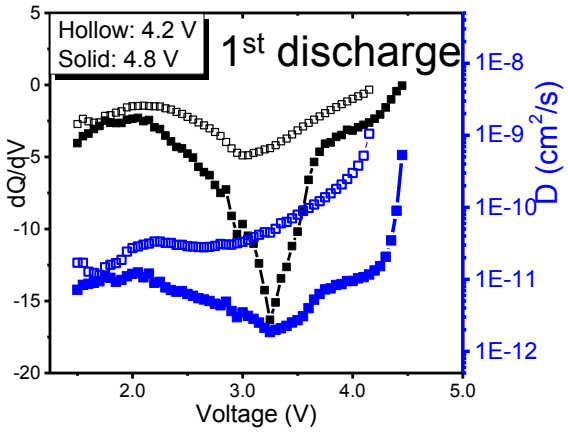
Summary

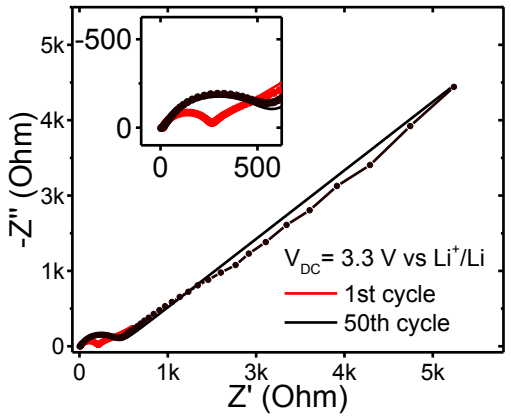
- Developed approaches to synthesize high-quality LRTM oxide model samples for diagnostic studies.
- Experimentally demonstrated the correlation in the extent of oxygen redox, charge storage capacity, cycling stability and rate capability of LRTM oxide cathodes.
- Elucidated the role of redox-inactive TM in modulating O redox activities, chemical stability and electrochemical performance of LRTM oxide cathodes.
- Investigated strategies to stabilize O redox and mitigate the capacity and stability trade-offs when utilizing oxygen redox process in LRTM oxide cathodes.

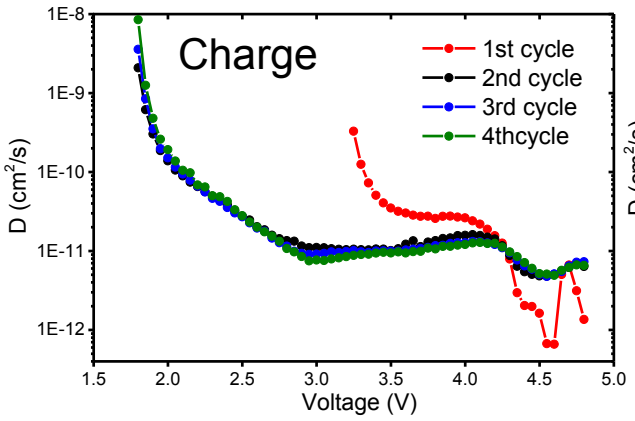
Technical Back-Up Slides

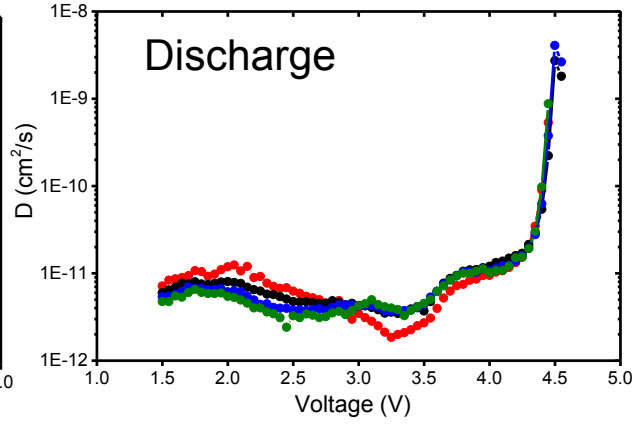
Rate capability correlated to extent of O redox

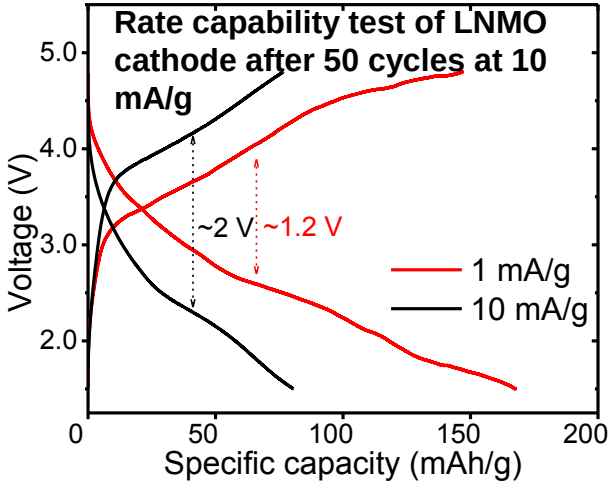






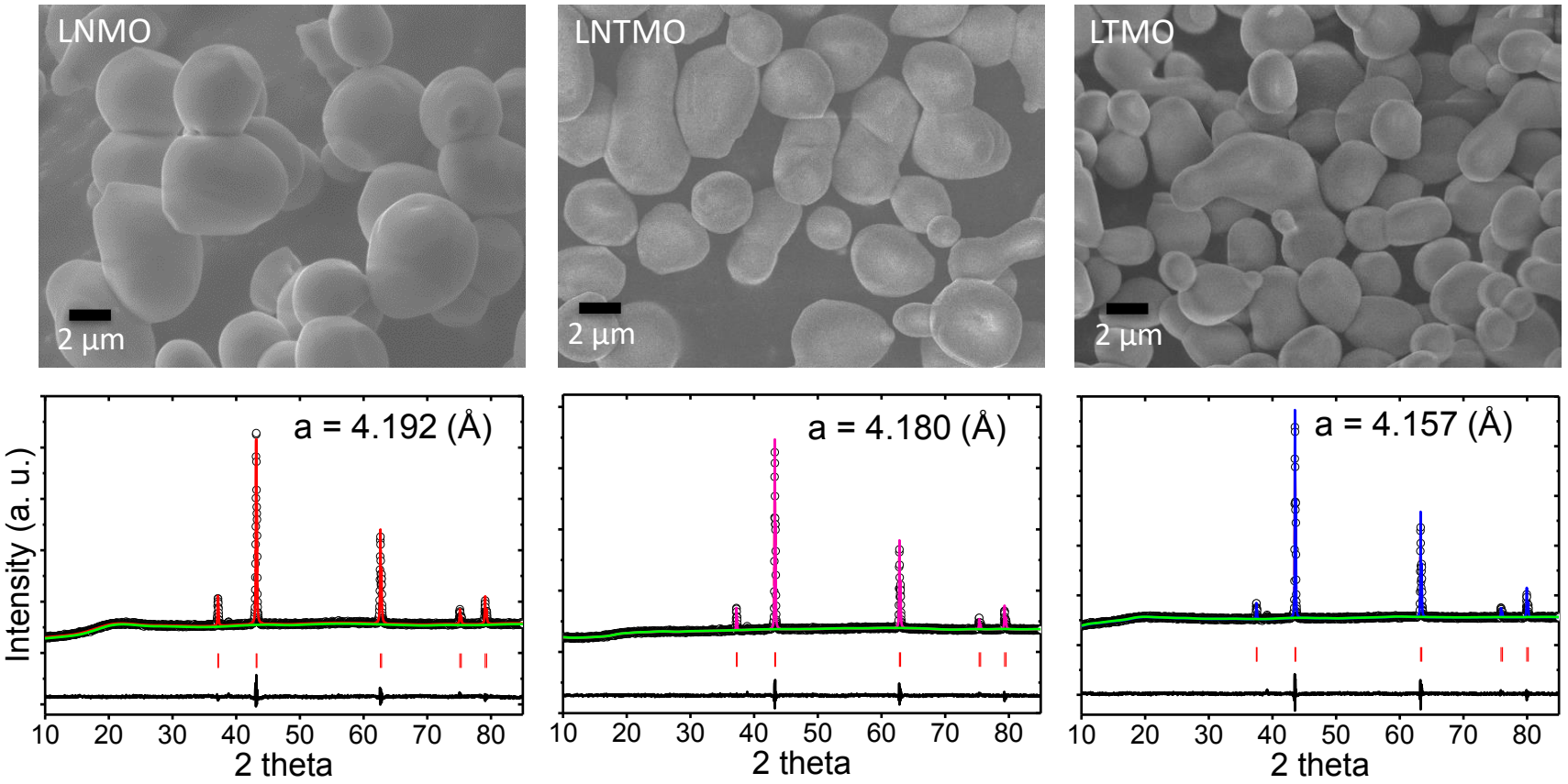






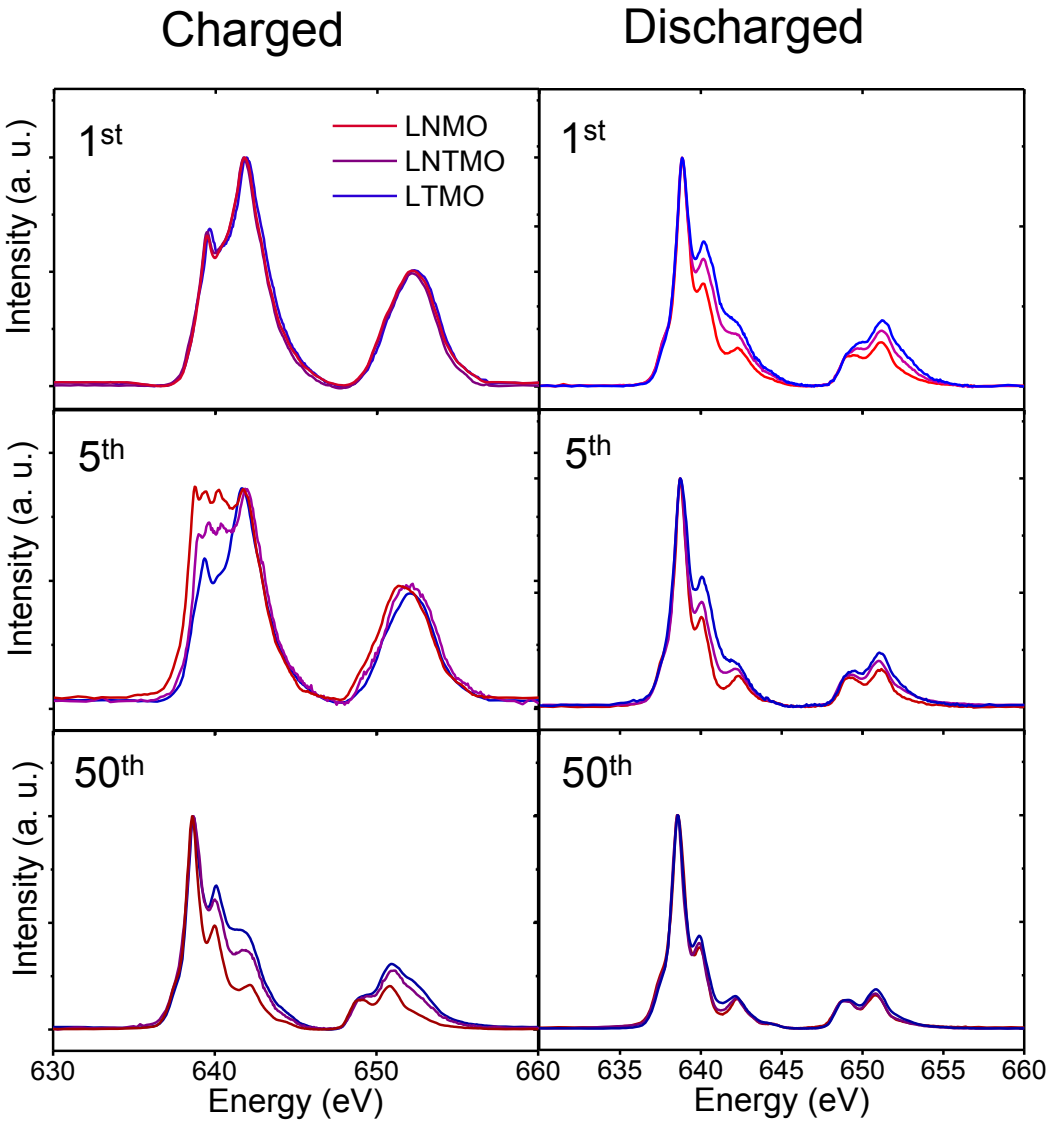
- Oxygen redox has poor kinetics and repeated cycling involving oxygen reduces TM redox kinetics as well.
- Significant capacity recovery at slower rate – kinetic barrier major source of degradation.

Pristine sample characterization



- LNMO, LNTMO and LTMO crystal samples are phase-pure rock-salts with similar size and morphology.

Redox-inactive TM influences surface chemical stability

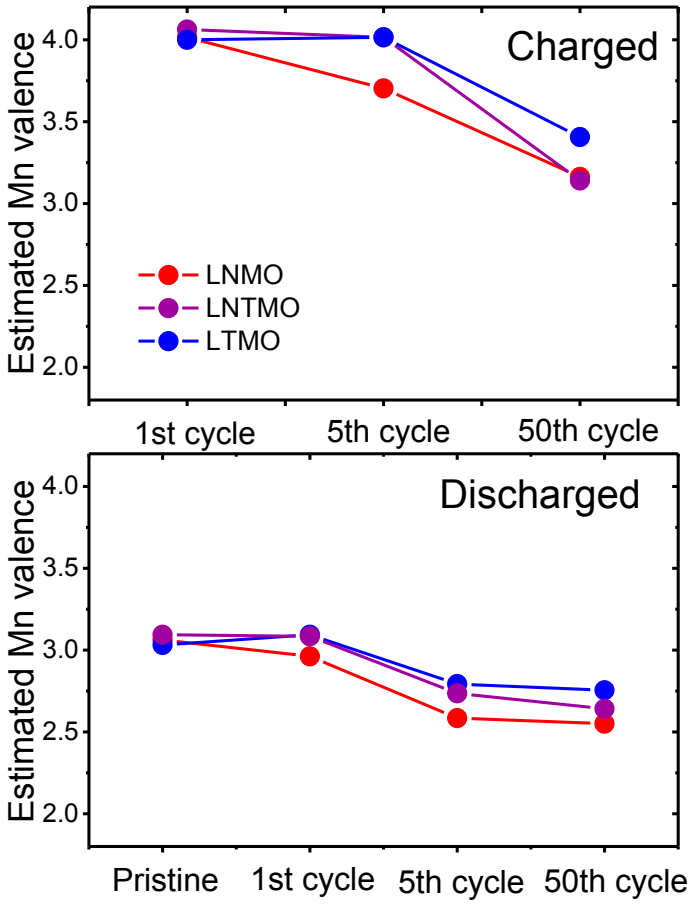


Mn L-edge TEY soft XAS
(SSRL beamline 8-2)

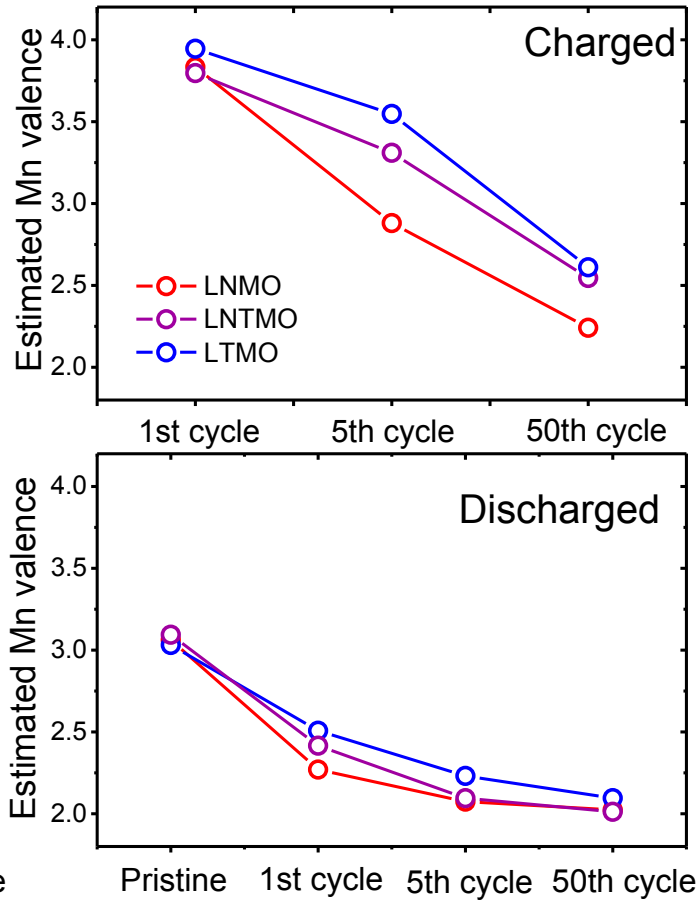
- Cycling leads to reduction of surface Mn in both LNMO and LTMO.
- Surface reduction less severe in LTMO than that in LNMO.

Effect of redox-inactive TM on surface and bulk chemical stability

Mn K-edge hard XAS
(SSRL beamline 2-2)



Mn L-edge TEY soft XAS
(SSRL beamline 8-2)



- Bulk and surface Mn oxidation states estimated from *K*-edge and *L*-edge X-ray absorption energies, respectively.
- With cycling, surface Mn more reduced than bulk.
- Ti shows stabilizing effect in both bulk and surface reduction.